THE INFLUENCE OF DETERGENTS ON THE LUMINESCENCE PROPERTIES OF RHODAMINE B AND 6 G IN AQUEOUS SOLUTION

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The influence of detergents on the quantum yield of fluorescence and on the dimerization process in lasing dyes e.g. Rhodamine B and 6 G in aqueous solution, has been determined. The effect of the concentration quenching of the fluorescence by energy migration versus the concentration of the detergent have been studied. The optimal detergent concentration for the laser generation is given.

Introduction

For a complete understanding of dye lasers, a knowledge of the absorption and emission properties of dyes in solvent is very helpful. Water, which has a high heat capacity, is a highly desirable solvent for laser dyes. It is known that organic dyes in aqueous solution have a tendency to form dimers [1-3]. The equilibrium between monomers and dimers in the solution shifts towards the latter with increasing dye concentration. The dimerization of dyes like Rhodamine B and 6 *G* at ambient temperature and concentration of 10^{-4} *M* is enough to prevent laser action. The non-fluorescent dimers absorb the pump light and increase the cavity losses. The cavity losses are due to their long-wave absorption band which overlaps the fluorescence spectrum of the monomers.

The detergents are added to the lasing dye solution to prevent the dye molecules to form dimers and increase the efficiency of laser generation.

The present work deals with the fluorescence quantum yield and degrees of dimerization of the Rhodamine B and 6 G in aqueous solution containing various amounts of the following detergents:

1. Hostapon $C_{12}H_{25}SO_4Na$
2. Sulfapol $C_{12}H_{25}C_6H_4SO_3Na$
3. Triton X-100 $C_8H_{17}-C_6H_4-O(OCH_2CH)_{10}H$

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Experimental

The quantum yield η of Rhodamine B and 6 G at $2 \cdot 10^{-5}$ M concentration in aqueous solution with various concentrations of the above detergents was measured using the apparatus described earlier [4]. The results are illustrated in Fig. 1. It can be seen in Fig. 1 that in the solution for which the concentration of detergents is below the critical micelle concentration (*c.m.c.*) the quantum yield is smaller than for pure water solution. If the detergent concentration is increased above the c.m.c., the quantum yield is larger than for the pure solution.

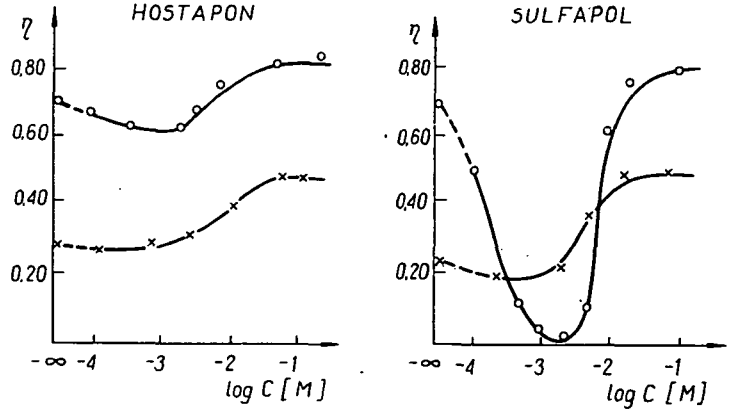

Fig. 1. The quantum yield of Rhodamine 6 G and Rhodamine B in aqueous solution versus the concentration of detergent. The dye concentration is $c = 2 \cdot 10^{-5}$ M

This effect was used for the determination of critical micelle concentration. The value of *c.m.c.* is about $3 \cdot 10^{-4}$ mol/l for Triton X-100 and 10^{-3} and $2 \cdot 10^{-3}$ mol/l for Hostapon and Sulfapol, respectively.

The quantum yield for solution at high dye concentration ($2 \cdot 10^{-4} - 2 \cdot 10^{-3}$ M) of Rhodamine B and 6 G was measured using a thin cuvette, in order to prevent reabsorption.

The fluorescence lifetime measurements for dye detergent solution were made by means of a phase shift fluoremeter [5].

The degree of dimerization of Rhodamine B and 6 G of this solution was calculated by means of the measured absorption spectrum [7-9].

The absorption spectra were recorded on a Zeiss-Jena type spectrophotometer using a quartz absorption cell with 0.01, 0.02, 1.0 cm path lengths. Fig. 2 shows the absorption spectra of Rhodamine B and 6 G in aqueous solution for $2 \cdot 10^{-3}$ M dye concentration at various concentrations of Triton X-100. It is noticable that 5% of Triton X-100 is enough to prevent Rhodamine dimerization.

Since the investigated solutions can be active media of dye lasers, it is useful to determine the lasing threshold. This was measured focusing the radiation from a nitrogen laser on a 1.0 cm cell containing the solution.

The results of the measurements as to the degree of dimerization (d), the relative value of the integrated intensity (f), and relative value of the lasing threshold (p) are illustrated in Fig. 3. As it can be seen from Fig. 3, if the detergent concentration increases, the degree of dimerization and the lasing threshold decreases but the fluorescence intensity increases. For both dyes, a volume concentration of 5% detergent increases the laser efficiency thus proving that this solution is a good laser medium.

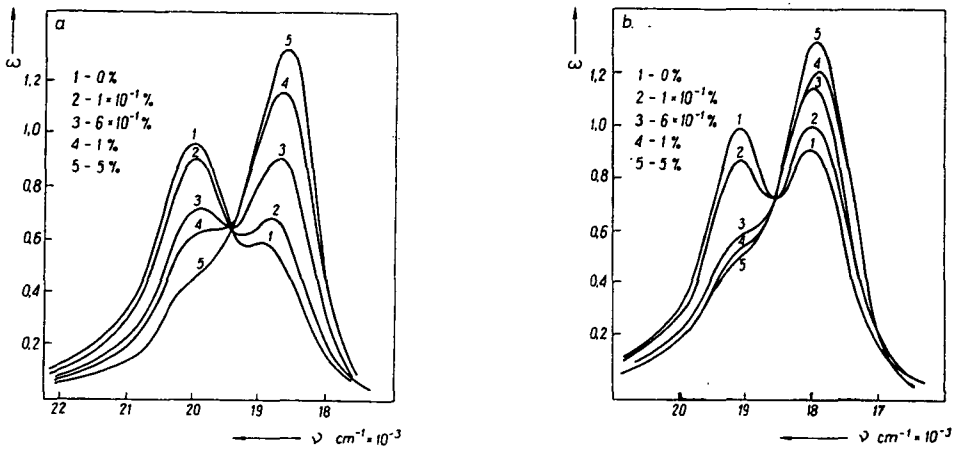

Fig. 2. Absorption spectra of Rhodamine B and 6 G in aqueous solution with various Triton X-100 concentration. Dye concentration is $c = 2 \cdot 10^{-3}$ M

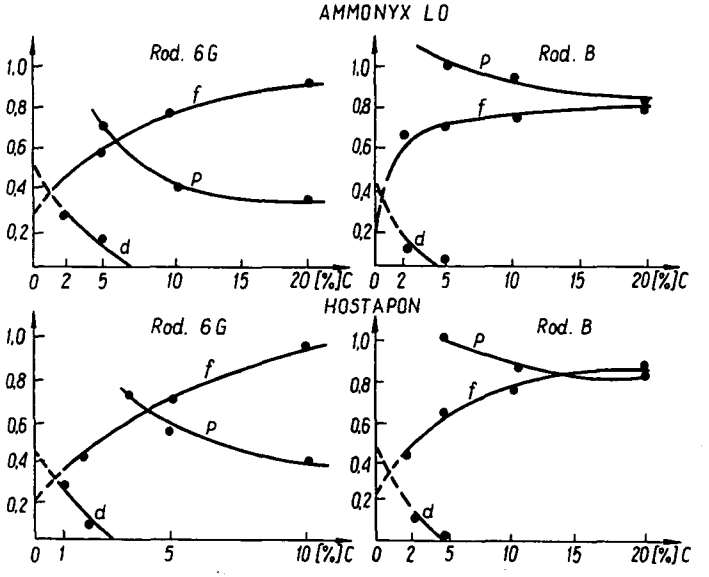

Fig. 3. The degree of dimerization d, relative value of the integrated lintensity f and lasing threshold p versus the detergent concentration. The concentration of Rhodamine B and 6 G was $c = 2 \cdot 10^{-3}$ M

Interpretation

In the region of critical detergent concentration the molecules of the dyes show the minimum quantum yield. This is due to the presence of insoluble dye-detergent complex salts in water.

The increase of quantum yield above the *c.m.c.* is due to the solubilization of the detergent complex salts [14].

The fact that the quantum yield of Rhodamine 6 G for aqueous solution without and with detergents increases from 0.71 to 0.80 is probably due to the solubilization of the dye dimers [7].

The quantum yield of Rhodamine 6 G in detergent solution increases almost by a factor of two. This increase cannot be explained in the same way as for the Rhodamine 6 G solution because the degree of dimerization of Rhodamine B at $2 \cdot 10^{-5}$ M dye concentration in aqueous solution is small.

The most important internal quenching mechanism for these dye molecules is connected with the mobility of the chromophore. In some xanthene dyes like Rhodamine B and Pyronine, potential mobility is connected with the mobility of the amino groups. The fluorescence efficiency of these dyes is reduced in most solvents (*e.g.* ethanol, water). The quantum yield can be increased considerably through the use of a solvent with strong molecular dipole moments which provide a microrigidity around the dye molecules [8].

The dye molecules introduced into the detergent solution are incorporated into micelles. The micelles strongly limit the mobility of the $N\langle^{Me}_{Me}$ groups in Rhodamine B which provide an increase in the quantum yield of these dyes.

The probability of nonradiative processes in Rhodamine B can be determined using the formula

$$W_{S_1S_0} + k_{ST} = (1-)\eta/\tau_f \tag{1}$$

where $W_{S_1S_0}$ and k_{ST} are the internal conversion rate and inter-system crossing rate respectively, τ_f is the mean lifetime of fluorescence.

Using the definition of the radiative transition probability given by the formula

$$A_{S_1S_0} = \eta/\tau_f \tag{2}$$

the influence of the detergent on the radiative processes $A_{S_1S_0}$ can be estimated. The results of the measurements and values of the estimated nonradiative and radiative transition rates of Rhodamine B in aqueous solution with various concentrations of Hostapon and Sulfapol are given in Table I.

It follows from Table I that the detergents prevent the nonradiative processes in Rhodamine B. For example, Sulfapol lowers the rate of the nonradiative processes by a factor of almost three.

Fig. 4 shows the dependence of the relative quantum yield and degree of monomerization of Rhodamine 6 G at $2 \cdot 10^{-4}$ M in aqueous solution with various concentration of Triton X-100. Knowing the molar absorption coefficient of the monomer $\varepsilon_M(\lambda)$ and dimer $\varepsilon_D(\lambda)$ for Rhodamine 6 G in aqueous solutions at excitation wavelength λ and the degree of monomerization X, one can determine the relative rate for "active" absorption.

"Active" absorption is defined as the ratio of the monomer absorption to the total absorption of the monomers and dimers as given by the following equation

$$\chi = \varepsilon_M X/\{\varepsilon_M + \varepsilon_D(1-X)/2\} \qquad (3)$$

Fig. 4 shows the dependence of χ versus the concentration of the detergents calculated using the formula (3). It follows from Fig. 4 that the χ curve does not fit to the curve of the relative quantum yield η/η_0. This can be explained by the effect of the concentration quenching of the fluorescence by energy migration.

This process is very effective for low detergent concentrations, since then, many dye molecules are incorporated into the same micelle. For solutions, where no concentration quenching processes appear, the relative quantum yield is equal to the "active" absorption. If the fluorescence is quenched by some processes then the dependence of η/η_0 versus χ is given by equation

$$\eta/\eta_0 = \chi \cdot \Phi \qquad (4)$$

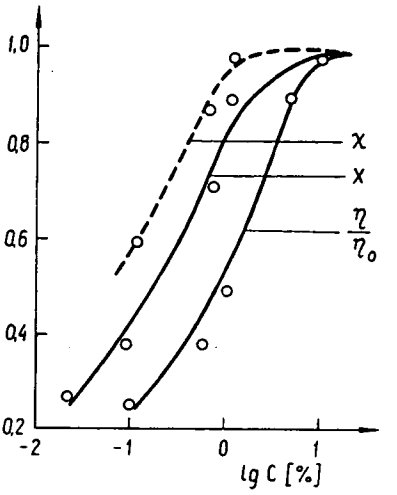

Fig. 4. The dependence of the relative value of quantum yield η/η_0, degree of monomerization X and the ratio of the monomer absorption to the total absorption of the monomer and dimer χ versus the Triton X-100 concentration. The concentration of Rhodamine 6 G is $c = 2 \cdot 10^{-4}$ M

where Φ describes the influence of all concentration quenching processes on the fluorescence quantum yield. If the quantum yield depends only on "active" absorption, the coefficient Φ is unity. From Fig. 4 it follows that the η/η_0 and χ curves differ and the differences are larger for higher detergent concentrations. As it can be seen from Fig. 4 the determined relative value of the quantum yield is three times smaller than the values of χ.

Table I

The τ_f and $W_{S_1S_0}+k_{ST}$ values of Rhodamine B ($2 \cdot 10^{-5}$ M aqueous solutions) versus different detergents concentration

	Detergent	c %	η	$\tau_f \cdot 10^{-9}$ s	$(W_{S_1S_0}+k_{ST}) \cdot 10^8$ s^{-1}
1.	Without detergent	—	0.25	2.1	3.6
2.	Hostapon	2	0.34	3.45	1.9
3.	Hostapon	5	0.41	3.55	1.6
4.	Hostapon	10	0.40	3.75	1.6
5.	Sufapol	2	0.43	3.9	1.4
6.	Sufapol	5	0.45	4.2	1.3

Summary

It has been shown that the quantum yield of Rhodanine B and 6 G depends on detergent concentration. Solutions with a detergent concentration below a critical value have a smaller quantum yield than pure aqueous solutions. This is due to the presence of insoluble dye-detergent complex salts. If the detergent concentration increases above the *c.m.c.*, the quantum yield increases also and reaches saturation for a detergent concentration of 10^{-2} M to 10^{-1} M.

The quantum yield for Rhodamine 6 G increases from 0.71 for pure aqueous solution to 0.80 for solution with detergent. The noted increase of η is due to the solublization of dye dimers. The quantum yield of Rhodamine B increases because the micelles strongly limit the mobility of the $N\begin{smallmatrix}Me\\Me\end{smallmatrix}$ groups in Rhodamine B. The detergents prevent the nonradiative processes in Rhodamine B almost by a factor of three.

Solution with high dye concentration and lower concentration of the detergent have a smaller quantum yield due to the concentration quenching of fluorescence by energy migration. From the performed investigations of the lasing threshold of Rhodamine B and 6 G at $2 \cdot 10^{-3}$ M in aqueous solution it follows that for both dyes a concentration of 5% detergent increases the laser efficiency thus proving that this solution is a good laser medium.

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ВЛИЯНИЕ ДЕТЕРГЕНТОВ НА ЛЮМИНЕСЦЕНТНЫЕ ХАРАКТЕРИСТИКИ РОДАМИНА Б И 6Ж В ВОДНОМ РАСТВОРЕ

З. Конефал

Исследовалось влияние детергентов на выход флюоресценции и на процесс димеризации в лазерных кристаллах таких как Родамин Б и 6 Ж в водном растворе.

Определен эффект концентрационного тушения флюоресценции как функции концентрации детергента.

Установлены оптимальные концентрации детергентов для лазерной генерации.